

FORMATION OF NEGATIVE IONS  
BY SURFACE IONIZATION

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF  
THE UNIVERSITY OF FLORIDA  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

August, 1966

#### ACKNOWLEDGMENTS

The author is extremely grateful to the chairman of his supervisory committee, Professor E. E. Muschitz, Jr., for his guidance and support, to Dr. A. S. Whiteman, who was responsible for the major construction of the apparatus, to Dr. David Stelman, for his helpful suggestions, aid in performing the experiments, and formulation of part of the theory presented in this dissertation, and to the other members of his supervisory committee for their suggestions in preparing the manuscript.

The author is also grateful to the National Aeronautics and Space Administration for the financial assistance which made this work possible.

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## INTRODUCTION

The phenomenon of surface ionization can occur when atoms or molecules from a gas or a vapor impinge upon an incandescent metal surface. After adsorption for a short period of time they may evaporate as neutral atoms, positive ions, or negative ions. Positive surface ionization occurs with high efficiency when the ionization potential of the incident species is less than the work function of the metal. Kingdon and Langmuir<sup>1</sup> first noted this effect in 1923. Negative surface ionization occurs when species with positive electron affinities capture electrons from the surface and evaporate as negative ions. Experimental observations of negative surface ionization were first made in 1935 by Sutton and Mayer.<sup>2</sup> Zandberg and Ionov<sup>3</sup> and Kaminsky<sup>4</sup> have presented rather thorough discussions on the subjects of positive and negative surface ionization. A recent review of electron affinities and various methods of their determination with 116 references has been written by Moiseiwitsch.<sup>5</sup>

Surface ionization has been used to solve various physical and technological problems. The detection of beams of alkali atoms and some of their compounds involved in reactive and non-reactive scattering experiments is one of the

principal uses of positive surface ionization. The ionization efficiency of the alkali metals is quite high at relatively low surface temperatures (about 1500° K.).

Determination of electron affinities by surface ionization has long been a field of great interest. Several factors make experimental negative ion current measurements difficult. Relatively high temperatures are required for negative ion emission, hence, thermionic electrons are also emitted and contribute to the negative ion current. The electrons may also form negative ions in gas phase collisions and thereby tend to obscure the effects of the surface ionization. Various methods, such as keeping the surface temperature low so the electron emission is small,<sup>6</sup> and suppressing the electrons with a magnetic field parallel to the cathode,<sup>2</sup> have been used to separate the effect of thermoelectrons from ion emission. The former method allows excessive contamination of the surface by gas atoms leading to erroneous results. Both methods require the assumption that the negative ion current is due to a single species. Mass spectrometric methods prove far superior to either of the above techniques since not only are the electron and ion beams separated but identification of the emitted ions is made possible. Attempts have been made to measure electron affinities of molecular ions by the magnetron method.<sup>7</sup> Many of the same experiments were carried out in a mass

spectrometer<sup>8</sup> and it was shown that the results of the magnetron experiments are almost entirely in error since only in a few cases is it possible to guess the identity of molecular ions emitted from a hot surface.

There are two types of mass spectrometric experiments by which electron affinities may be determined by surface ionization. Both are measurements of equilibrium constants.<sup>9,10</sup> One type involves the measurements of emission of positive ions, negative ions, and electrons from a hot surface upon which impinges vaporized alkali metal salts. Since essentially all of the alkali atoms leave the surface as positive ions and the anions leave the surface as neutral species, the current of the neutrals is given by the positive ion current. The electron current and the negative ion current are measured separately; hence the equilibrium constant for the electron attachment reaction, which is directly related to the electron affinity, may be obtained. The second method, the method used in this work, is the determination of electron affinity differences. This method involves the measurement of the currents of negative ions emitted from a hot surface when molecules containing two electronegative species are incident upon the surface. The ratio of the negative ion currents is related to the difference in the electron affinities of the two species.

Most electron affinity difference determinations involve a hot filament surrounded by gas containing the electronegative species. Bailey,<sup>9</sup> in his experiments, used a diffuse beam of interhalogen compounds incident upon a tungsten wire to arrive at the difference in the electron affinities of two halogens. Bakulina and Ionov<sup>10</sup> used two molecular beams of alkali metal salts with the same cation but different anions incident upon the same portion of a tungsten filament to determine electron affinities of the halogens, sulphur, and the cyanide radical by differences. In this work a well-collimated molecular beam is incident upon a small portion of a tungsten ribbon filament so that there should be a negligible temperature gradient across the beam-surface interface. The purpose of these experiments is to explore the feasibility of using polyatomic molecules containing two electronegative species (both atomic and molecular) for the determination of electron affinity differences, and to examine the extent of dissociation of such molecules on a hot tungsten surface as a function of the surface temperature.

## THEORY

The electron affinity of an atom or molecule is defined as the energy at 0°K for the electron attachment reaction,



This quantity may be determined from a measurement of the equilibrium constant,  $K_P$ , for the reaction. For (1) at equilibrium

$$\ln K_P = \ln(P_{X^-}/P_X P_e) = -\Delta F^0/RT \quad (2)$$

or

$$RT \ln K_P = -E(X) + F_e^{(0)} + F_X^{(0)} - F_{X^-}^{(0)} \quad (3)$$

where  $F_i^{(0)}$  are the free energies of the reactants and products at temperature T and one atmosphere pressure chosen so that they are zero at 0°K and  $P_i$  equal to one atmosphere. The partial pressures,  $P_i$ , may be calculated from the numbers  $Z_i$ , of species i being emitted per unit area per unit time from a hot surface at temperature T from the relation

$$P_i = Z_i (2\pi m_i kT)^{1/2} \quad (4)$$

where  $m_i$  are the masses of species i and k is the Boltzmann constant.

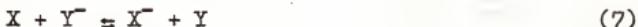
If a molecule such as  $RX_mY_n$  or  $X_mY_n$  containing two electronegative species dissociates on a hot surface according to



or



equilibrium between the two electronegative species emitted from the surface will exist as



for (7),

$$-\Delta F^0/RT = \ln K_p = \ln (Z_{X^-}/Z_X)(Z_Y/Z_{Y^-}) \quad (8)$$

and

$$-\Delta F^0 = E(X) - E(Y) + (F_X^{(0)} - F_{X^-}^{(0)}) - (F_Y^{(0)} - F_{Y^-}^{(0)}) \quad (9)$$

From statistical mechanics, the free energy is given by

$$F = -kT \ln Q^0 + kT V(\partial \ln Q^0 / \partial V) \quad (10)$$

where  $Q^0$  is the total partition function for a canonical ensemble of  $N$  systems and

$$Q^0 = (1/N!)(q_{trans}^N q_{rot}^N q_{vib}^N q_{elec}^N) = (1/N!)(q_{trans}^N Q^N) \quad (11)$$

The  $q$ 's are the translational, rotational, vibrational,

and electronic partition functions, and  $Q$  denotes the "internal" partition functions. For translation,

$$q_{\text{trans}} = V(2\pi mkT/h^2)^{3/2} \quad (12)$$

Substituting (12) with (11) into (10), making use of Stirling's approximation for large  $N$  ( $\ln N! = N \ln N/e$ ) and using  $PV = NkT$  (10) becomes

$$F = RT \left\{ \ln \left[ (P/kT) \left( h^2/2\pi mkT \right)^{3/2} \right] - \ln Q \right\} \quad (13)$$

Since  $F_i^{(0)}$  are measured at one atmosphere pressure (13) may be written

$$F_i^{(0)} = RT \left\{ \ln \left[ (1/kT) \left( h^2/2\pi m_i kT \right)^{3/2} \right] - \ln Q_i \right\} \quad (14)$$

Substituting (14) with (9) into (8) yields the difference in the electron affinities of  $X$  and  $Y$ :

$$E(X) - E(Y) = RT \ln \left[ \left( Z_{X^-}/Z_X \right) \left( Z_Y/Z_{Y^-} \right) \left( Q_{Y^-}/Q_Y \right) \left( Q_X/Q_{X^-} \right) \right] \quad (15)$$

$Z_{X^-}/Z_{Y^-}$  is simply the ratio of the emitted ion currents.

$Z_Y/Z_X$  is the ratio of the numbers of  $Y$  and  $X$  atoms leaving the surface or the ratio of their concentrations on the surface and is equal to  $n/m$  since  $Z_{X^-} \ll Z_X$  and  $Z_{Y^-} \ll Z_Y$ . Hence

$$E(X) - E(Y) = RT \ln \left[ (n/m) \left( I_{X^-}/I_{Y^-} \right) \left( Q_X/Q_Y \right) \left( Q_{Y^-}/Q_{X^-} \right) \right] \quad (16)$$

The slope of a plot of  $\ln[(I_X^-/I_Y^-)(Q_X/Q_Y)(Q_Y^-/Q_X^-)]$  vs  $1/T$  gives the electron affinity difference. The intercept at  $1/T = 0$  gives  $m/n$  if X and Y are atoms and if the dissociation on the surface is complete. The derivation of (16) follows that given by Bailey.<sup>9</sup>

If the assumptions made in arriving at equation (16) are correct, the ratio of the ion currents is independent of the work function of the surface and the beam flux incident upon the surface. It must also be assumed that the accommodation coefficients for electron exchange between the surface and X and Y species on the surface are unity.

For atoms, only the electronic partition functions must be included in (16). These are given by

$$q_{elec} = g_0 + \sum g_j \exp(-E_j/kT) \quad (17)$$

where  $g_0$  and  $g_j$  are the degeneracies of the ground and  $j^{\text{th}}$  excited states, respectively, and  $E_j$  is the difference in the energies of the two states. Fluorine and chlorine, for example, both have a low-lying  $^2P_{1/2}$  excited state of energies above the  $^2P_{3/2}$  ground state corresponding to 404 and  $881 \text{ cm}^{-1}$ , respectively. The ions in their ground states possess  $^1S_0$  configurations and presumably have no low-lying excited states. Hence the ratio of fluorine to chlorine partition functions is

$$Q_F/Q_{Cl} = [4+2 \exp(-404 \times 1.439/T)]/[4+2 \exp(-881 \times 1.439/T)] \quad (18)$$

and the ratio of the partition functions of the ions is unity.

In the case of molecules or radicals, the vibrational and rotational partition functions as well as the electronic partition functions must be taken into consideration. For a harmonic oscillator the vibrational partition function is.

$$q_{vib} = 1/[1 - \exp(-hc\omega/kT)] \quad (19)$$

where  $\omega$  is the vibrational frequency in  $\text{cm}^{-1}$ ,  $h$  is Planck's constant, and  $c$  is the speed of light in a vacuum. The quantity  $hc\omega$  is the vibrational energy relative to the energy of the ground vibrational state. There exists one such term for each normal mode of vibration in the molecule. Using a rigid rotor model the rotational partition function for a linear molecule is given by

$$q_{rot} = (1/\sigma)(kT/hcB) \quad (20)$$

The quantity  $\sigma$  is the symmetry number which is the number of indistinguishable orientations of the molecule in space and  $B$  is the rotational constant which is equal to  $(h/8\pi^2Jc)$  where  $J$  is the moment of inertia of the molecule. For non-linear molecules

$$q_{rot} = (\pi^{1/2}/\sigma)(kT/hcB_x)^{1/2}(kT/hcB_y)^{1/2}(kT/hcB_z)^{1/2} \quad (21)$$

where  $B_x$ ,  $B_y$ , and  $B_z$  are the rotational constants corresponding to the three principal moments of inertia of the non-linear molecule.

Vibrational and rotational constants are known for many molecules and radicals<sup>11</sup> but very little is known about these quantities for negative ions. From surface ionization it is possible to learn much about the rotation and vibration of negative ions. Consider, for example, the CN radical and the CN<sup>-</sup> ion. The radical possesses a  $^2\Sigma^+$  electronic configuration with a ground state degeneracy of 2 and the ion probably possesses a  $^1\Sigma$  configuration with a ground state degeneracy of 1. For both species the electronic partition function is approximately the degeneracy of the ground state since no low-lying excited states are available. The first electronically excited state of the CN radical occurs at an energy corresponding to 9242  $\text{cm}^{-1}$  above the ground state.<sup>12</sup> The vibrational partition functions are given by equation (19) and the rotational partition functions are given by equation (20). The ratio of the internal partition function of the ion to that of the radical is

$$Q_{\text{CN}^-}/Q_{\text{CN}} =$$

$$(1/2)(B_{\text{CN}}/B_{\text{CN}^-}) [1-\exp(-hc\omega_{\text{CN}}/kT)]/[1-\exp(-hc\omega_{\text{CN}^-}/kT)]$$

(22)

Equation (22) may be put into more convenient form using the following considerations. The vibrational frequency of the ion is equal to that of the radical plus some increment,  $\epsilon$ . That is

$$\omega_{\text{CN}^-} = \omega_{\text{CN}} + \epsilon \quad (23)$$

Expanding  $1 - \exp[-a(\omega + \epsilon)]$ , where  $a = hc/kT$  and  $\omega = \omega_{\text{CN}}$ , using a Taylor series expansion, gives

$$\begin{aligned} 1 - \exp[-a(\omega + \epsilon)] &= [1 - \exp(-a\omega)] + \\ &[\exp(-a\omega)](a\epsilon - a^2\epsilon^2/2! + \dots) \end{aligned} \quad (24)$$

and

$$\begin{aligned} (\text{q}_{\text{vib}})_{\text{CN}^-}/(\text{q}_{\text{vib}})_{\text{CN}} &= \{1 - \exp[-a(\omega + \epsilon)]\} / [1 - \exp(-a\omega)] = \\ &1 + \{1 / [\exp(a\omega) - 1]\} (a\epsilon - a^2\epsilon^2/2! + \dots) \end{aligned} \quad (25)$$

At 2000° K, letting  $\epsilon$  be equal to 10 per cent of  $\omega_{\text{CN}}$ , and keeping only the leading term in the series introduces an error of only 1 percent. Therefore, assuming  $\epsilon$  is small,

$$(\text{q}_{\text{vib}})_{\text{CN}^-}/(\text{q}_{\text{vib}})_{\text{CN}} = \{1 + a\epsilon / [\exp(a\omega) - 1]\}^{-1} \quad (26)$$

The rotational constant of the  $\text{CN}^-$  ion is that of the radical plus an increment,  $\beta$ .

$$B_{\text{CN}^-} = B_{\text{CN}} + \beta \quad (27)$$

and

$$(q_{\text{rot}})_{\text{CN}^-}/(q_{\text{rot}})_{\text{CN}} = B_{\text{CN}}/B_{\text{CN}^-} = [1 + \beta/B_{\text{CN}}]^{-1} \quad (28)$$

Then the ratio of the internal partition functions becomes

$$Q_{\text{CN}^-}/Q_{\text{CN}} = (1/2)(1 + \beta/B_{\text{CN}})^{-1} \{ 1 + a\epsilon / [\exp(a\omega)] \}^{-1} \quad (29)$$

and

$$\ln(Q_{\text{CN}^-}/Q_{\text{CN}}) = -\ln 2 - \ln(1 + \beta/B_{\text{CN}}) - \ln \{ 1 + a\epsilon / [\exp(a\omega) - 1] \} \quad (30)$$

Now making use of the relation

$$\ln(1 + x) = x - x^2/2 + x^3/3 - \dots \quad (-1 < x < 1) \quad (31)$$

and keeping only the first term in the series, (30) becomes

$$\ln(Q_{\text{CN}^-}/Q_{\text{CN}}) = -\ln 2 - (\beta/B_{\text{CN}}) - (hc/kT) \{ \epsilon / [\exp(hc\omega_{\text{CN}}/kT) - 1] \} \quad (32)$$

Since vibrational and rotational constants for the CN radical and for many other molecules are known, only  $\beta$  and  $\epsilon$  are left to be evaluated. This may be done by using a compound containing an atomic and a molecular electronegative constituent. The intercept at  $1/T = 0$  of a plot of the logarithm of the ion current ratio versus the reciprocal of the absolute temperature should give the second term in the right-hand side of (32). From any non-linearity in the plot

the last term could be calculated and at least an upper limit set on the difference in the vibrational frequencies of the radical and the ion.

## EXPERIMENTAL

### Description of the Apparatus

The surface ionization apparatus used in this work is shown schematically in Figure 1. It consists of a molecular beam source (chamber 1), two collimating chambers (chambers 2 and 3), a reaction chamber (chamber 4), and a 3-inch radius of curvature, 90° sector, magnetic deflection mass spectrometer. All of the chambers, with the exception of the mass spectrometer analyzer tube, are fabricated of stainless steel. The analyzer tube is a 90° section of silver wave guide whose inside dimensions are 0.900 inches by 0.400 inches. The overall length of the apparatus is about 18 inches and the diameter of chambers 2, 3, and 4 is 4 inches.

Chambers 2, 3, and 4 and the analyzer tube are all separately pumped. Chamber 4 may be baked out at temperatures of about 200° C. Background pressures in the reaction chamber with the filament at operating temperature after several hours of baking, are about  $10^{-7}$  torr. Chambers 2 and 3 and the analyzer tube are pumped at ports D by Consolidated Vacuum Corporation, PMC 115, oil diffusion pumps which have pumping speeds of 100 liters per second. The diffusion pumps are attached to Welch, Model

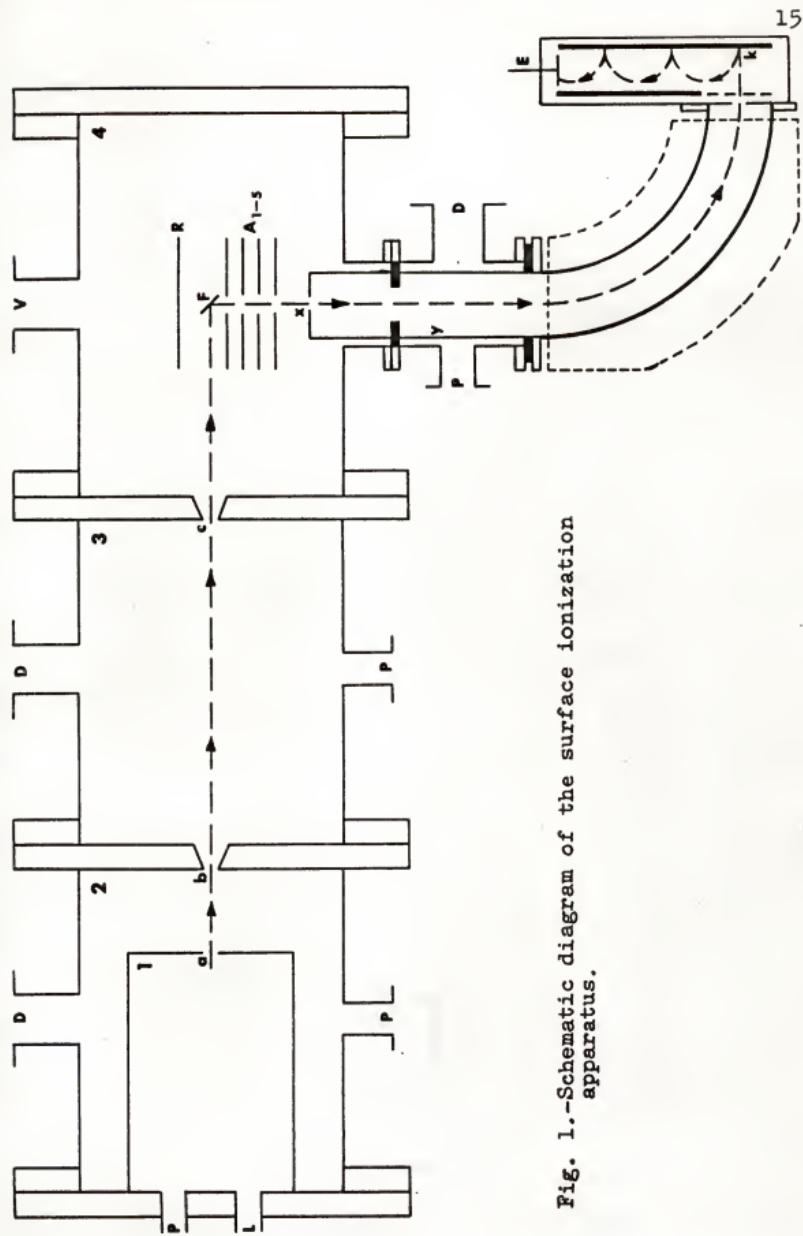


Fig. 1.—Schematic diagram of the surface ionization apparatus.

1402B, mechanical pumps which have pumping speeds of 100 liters per minute. The reaction chamber is pumped at port V with a Varian VacIon pump whose pumping speed is 15 liters per second. The pressure may be monitored in each section of the apparatus at ports denoted by P. In chambers 1 and 2 the pressure is measured using Consolidated Vacuum Corporation Autovac Piranini gauges. Pressures in chamber 3 and the analyzer tube region are measured with Vacuum Electronics Corporation ionization gauges. The pressure in the reaction chamber is monitored at all times by measuring the ion current, which is calibrated in torr, to the cathode of the VacIon pump.

#### Operation

Gas is introduced into chamber 1, Figure 1, at L. It effuses out of a 1/2 mm orifice at (a) and is collimated by 1 mm and 3/4 mm orifices at (b) and (c), respectively. The collimated beam then impinges upon a heated polycrystalline tungsten ribbon filament F. The total path length of the beam is 11 inches; 2 inches between (a) and (b), 6 inches between (b) and (c), and 3 inches between (c) and F. The ions evaporated from the surface are accelerated and focused by a series of electrodes R and A<sub>1-5</sub>. The ion beam then strikes the mass spectrometer entrance slit at (x), traverses a field-free region (y), and after mass analysis

strikes the cathode (k) of a Bendix magnetic electron multiplier. The output currents of the electron multiplier are measured with a Keithley, Model 603, electrometer amplifier and recorded by a Leeds and Northrup Speedomax G recorder. The lower limit of ion current measurements is approximately  $10^{-16}$  amperes.

A beam shutter located in chamber 3, Figure 1, allows interruption of the molecular beam so that the background ion currents which are due to both surface ionization and electron bombardment of the residual gas in the reaction chamber may be measured.

#### Description of the Ion Source

Figure 2 is a detailed, full-scale drawing of the ion source. The electrodes R and  $A_{1-5}$  are constructed of stainless steel plate. The tungsten ribbon filament, located at F, is spot welded between platinum tabs which are fastened to the filament supports, S, by molybdenum screws. The filament supports are made of nickel. The electrodes are aligned by placing Pyrex rods through holes in each corner of the plates and are separated by spacers of quartz tubing. The rest of the ion source is made of stainless steel.

The molecular beam, indicated by the arrow in Figure 2, is incident upon the hot filament which is heated by a low voltage, high current, 60 cycle AC power supply. The

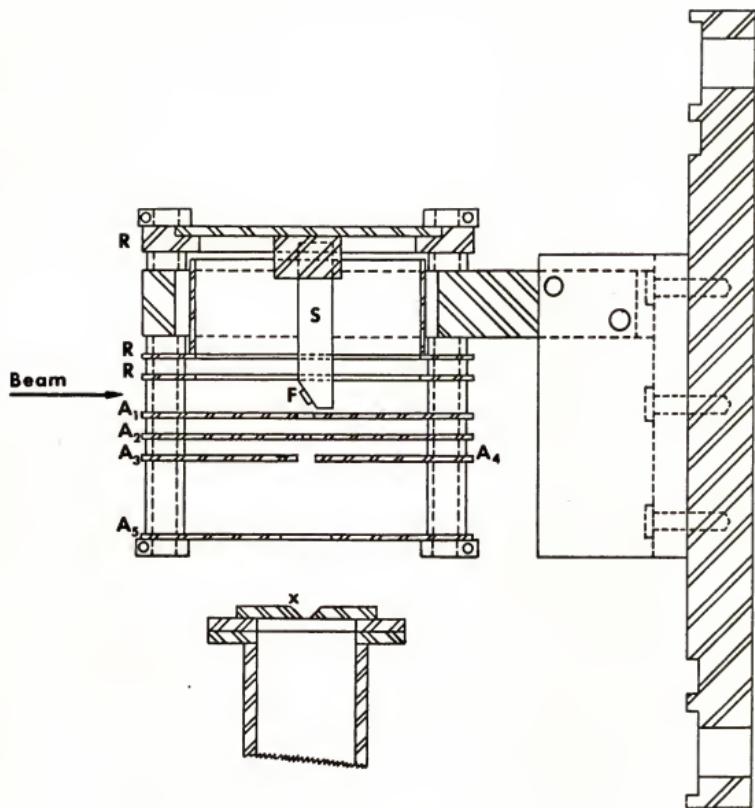


Fig. 2.-Full-scale drawing of the ion source.

input voltage to this power supply is regulated to within 0.05 per cent by a Sorenson, Model 1000S, line voltage regulator. The ions evaporated from the filament are repelled by the field set up by electrodes R, extracted by  $A_1$ , accelerated and focused by  $A_2$ ,  $A_3$ ,  $A_4$ , and  $A_5$ , and enter the mass spectrometer at (x). The potential may be varied on R from 0 to -5 volts, on  $A_1$  from 0 to 10 volts, and on  $A_2$  from 10 to 65 volts.  $A_3$  and  $A_4$  are the focusing electrodes and each has voltages applied to them which are separately variable between 65 and 220 volts with respect to the filament potential.  $A_5$  and (x) may have equal potentials of 500, 800, or 1000 volts with respect to the filament applied to them. Typical operating potentials, measured with respect to the filament, are: R = -5 volts,  $A_1$  = 2 volts,  $A_2$  = 65 volts,  $A_3$  =  $A_4$  = 150 volts, and  $A_5$  = (x) = 1000 volts. A schematic diagram of the electrical circuitry involved in operating various parts of the apparatus is shown in Figure 3. In Figure 3,  $P_1$  is a rectified RF high voltage DC power supply,  $P_2$  and  $P_3$  are Acopian transistorized DC power supplies whose output voltages are 70 and 150 volts, respectively.  $P_4$  is a Kepco, Model ABC 2500M, DC power supply with a continuously variable output between 0 and 2500 volts.  $P_4$  supplies the voltage across the voltage divider for the electron multiplier B and supplies the same potential to  $A_5$ , the entrance slit and

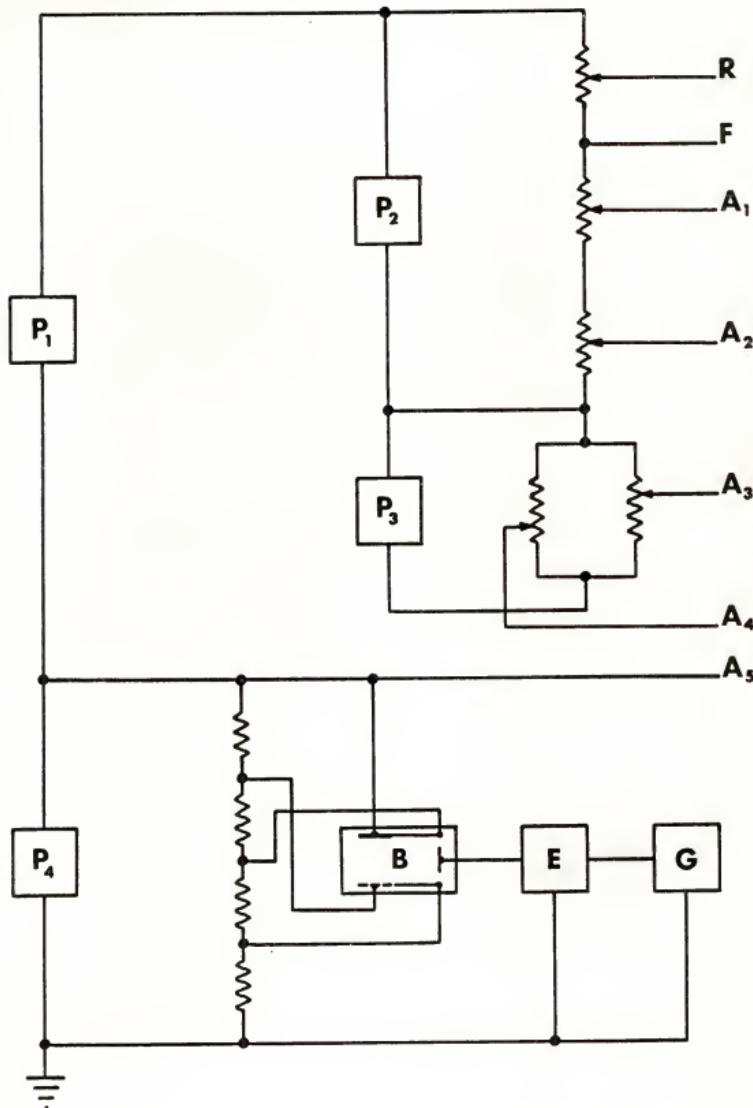


Fig. 3.-Schematic diagram of the electrical circuitry.

analyzer tube of the mass spectrometer, and the positive side of  $P_1$ .  $P_1$ ,  $P_2$ , and  $P_3$  are line and load regulated to within 0.05 per cent and  $P_4$  is line and load regulated to within 0.01 per cent.  $E$  is the electrometer amplifier and  $G$  is the recorder.

#### Experimental Measurements

The pressure of the reactant gas is raised to 0.5 to 1.0 torr in the beam source (chamber 1, Figure 1) and a molecular beam is formed which strikes the target filament. The ions are extracted from the filament, accelerated, and focused upon the entrance slit of the mass spectrometer. The ion energy upon entrance to the mass spectrometer is 1000 electron volts. The magnetic field is swept automatically with the beam shutter open and then with the shutter closed. In this manner it is possible to determine which peaks are due to surface ionization of species in the molecular beam, which peaks are due to the ionization of background gasses, and to determine background corrections for the ion currents. The two peaks of interest are swept at a speed of about one mass unit in 15 seconds. One peak is swept, then the magnetic field is changed manually to a point where the next peak can be swept without a great deal of time loss between successive peak measurements. The ion intensity ratio, corrected for background and isotopic

contributions, is taken as a function of the filament temperature.

The temperature measurements are made by sighting on the filament through an optically flat, Pyrex window with a Leeds and Northrup, Model 8622C, optical pyrometer which is of the disappearing filament type. The pyrometer and viewing port are shown in the photograph of the apparatus in Figure 4. The temperature thus obtained is the brightness temperature of the filament and must be converted to the true temperature. This is done using tables from the Handbook of Chemistry and Physics.<sup>13</sup>

The magnetic field measurements are made using a Rawson-Lush, Type 720S, rotating coil gaussmeter.

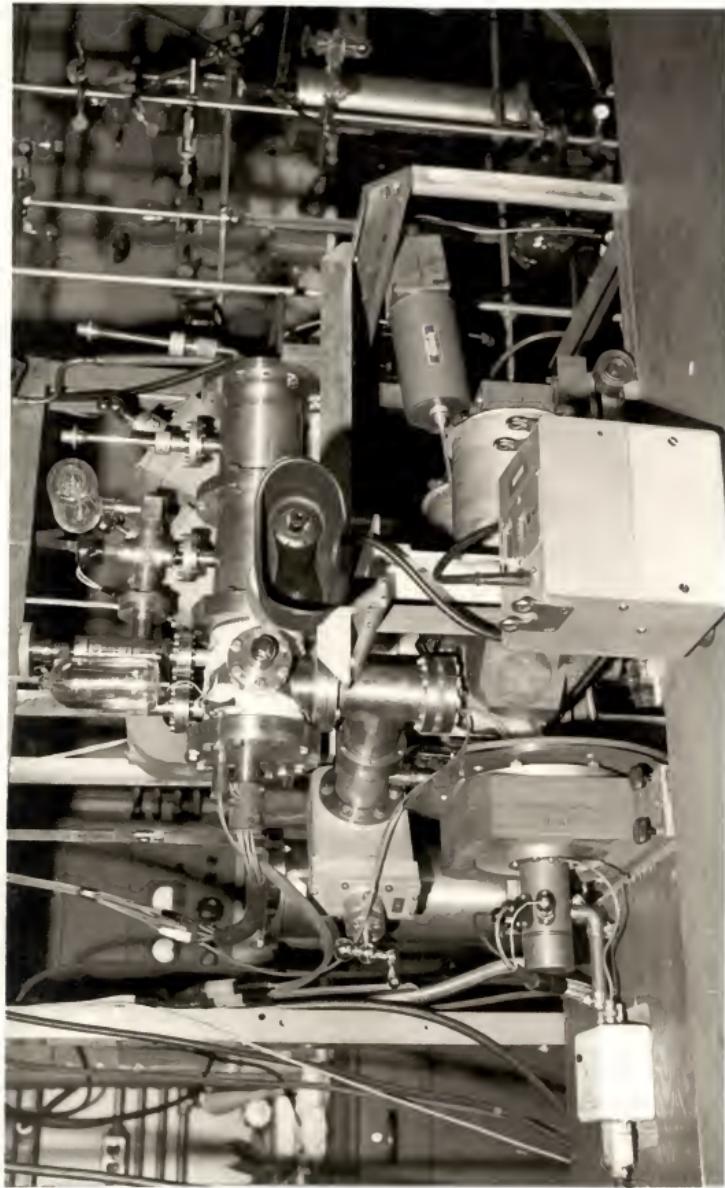


Fig. 4.-Photograph of the surface ionization apparatus.

## RESULTS

### Chlorine

In the preliminary tests of the apparatus a beam of chlorine molecules was allowed to impinge upon the tungsten filament and the  $\text{Cl}^-$  ion intensity was taken as a function of the surface temperature. Figure 5 is a plot of the  $\text{Cl}^-$  ion current versus the reciprocal of the absolute surface temperature. The plot shows a maximum at a surface temperature of about  $2030^\circ \text{ K}$ . All of the ions observed in these experiments exhibited the same behavior, that is, they all showed a maximum intensity at about the same temperature.

### Freons

In the mass spectra of the Freon series,  $\text{CF}_3\text{Cl}$ ,  $\text{CHF}_2\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ , and  $\text{CFCl}_3$ , peaks were observed at  $m/e$  of 16, 19, 35, and 37. Mass 16 ( $\text{O}^-$ ) arises from electron bombardment of the background gas and oxides on the filament. Masses 19, 35, and 37 are  $\text{F}^-$ ,  $(\text{Cl}^{35})^-$ , and  $(\text{Cl}^{37})^-$ , respectively. The  $(\text{Cl}^{37})^-$  to  $(\text{Cl}^{35})^-$  ratio is  $1/3$  in all cases.

Figure 6 shows a semilogarithmic plot of  $I_{\text{F}^-}/I_{\text{Cl}^-}$  versus the reciprocal of the absolute surface temperature

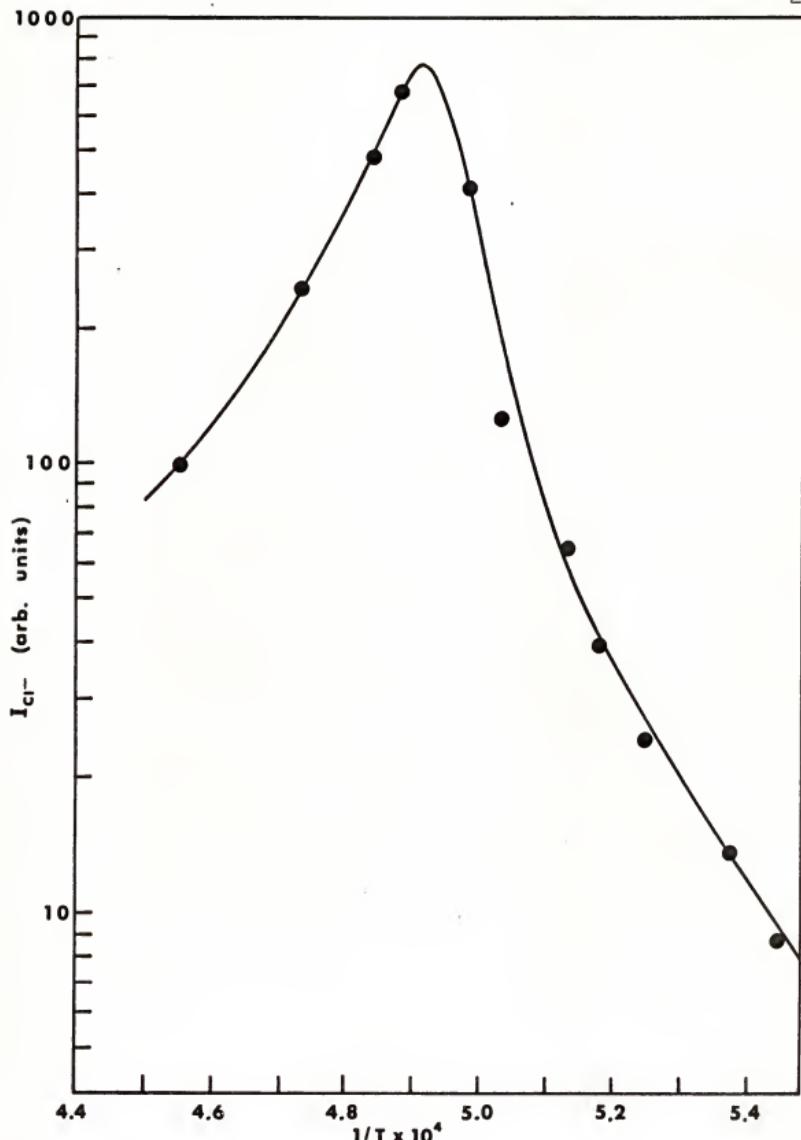


Fig. 5.- $I_{Cl^-}$  versus reciprocal of absolute surface temperature for chlorine.

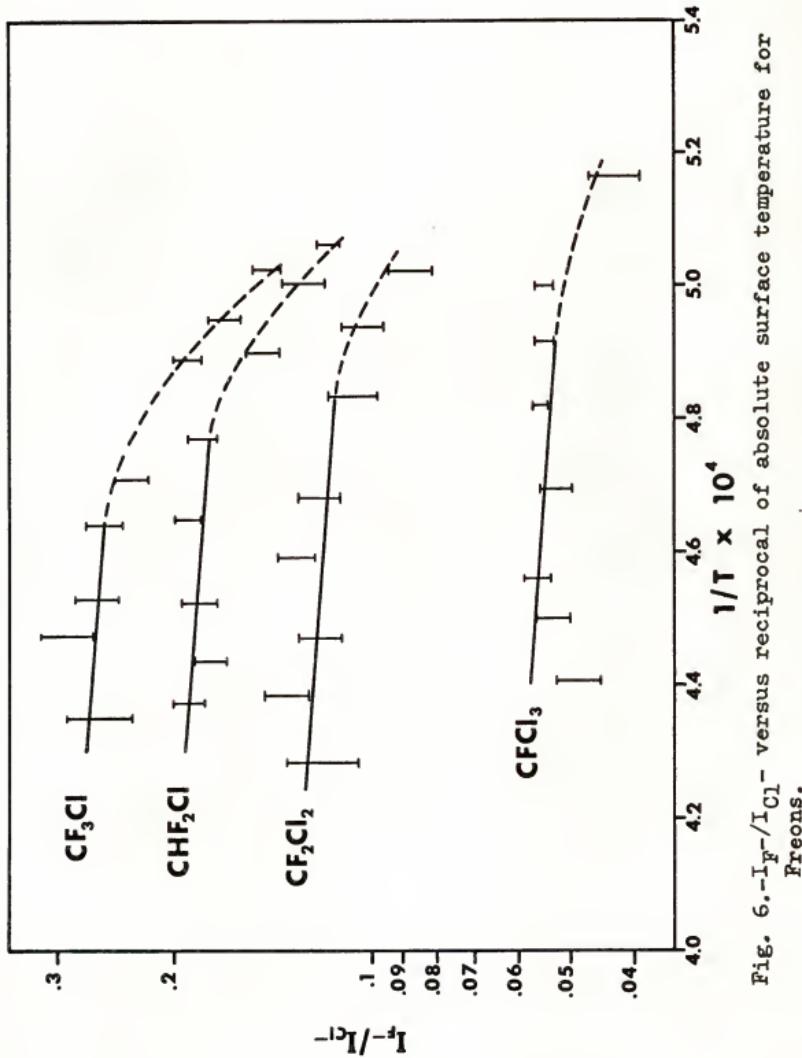


Fig. 6.  $-I_F^-/I_{Cl^-}$  versus reciprocal of absolute surface temperature for Freons.

for  $\text{CF}_3\text{Cl}$ ,  $\text{CHF}_2\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ , and  $\text{CFCl}_3$ . The F to Cl partition function ratio is nearly constant over the range of temperatures investigated and contributes little to the ion current ratio. The straight lines are assigned a slope corresponding to  $E(\text{Cl}) - E(\text{F})$  equal to 0.20 electron volts as reported by Bailey<sup>9</sup> and are fitted to the experimental points at high temperatures by the method of least squares. The plots indicate the correct trend of the intercepts at  $1/T = 0$  to higher values of  $m/n$  as the F to Cl atom ratio increases in the molecules. However, the intercepts are far below the values expected from equation (16) if the molecules are completely dissociated on the surface. Table 1 gives the theoretical values of  $m/n$  and the observed values in these experiments.

TABLE 1  
THEORETICAL AND OBSERVED VALUES OF  $m/n$  IN FREONS

$\text{CF}_m\text{Cl}_n$	$(m/n)_{\text{theory}}$	$(m/n)_{\text{obs.}}$
$\text{CF}_3\text{Cl}$	3	0.56
$\text{CHF}_2\text{Cl}$	2	0.35
$\text{CF}_2\text{Cl}_2$	1	0.23
$\text{CFCl}_3$	$1/3$	0.12

No peaks corresponding to undissociated fragments of the molecules (e.g.  $\text{CF}^-$ ) were observed. Also, a search for ions of the type  $\text{WF}_x^-$  was made without success. If such ions are emitted from the surface, then the electron affinities of the radicals must be  $< 3$  electron volts.

#### Chloroacetonitrile

The mass spectrum due to surface ionization of chloroacetonitrile ( $\text{CH}_2\text{ClCN}$ ) showed peaks at  $m/e$  of 16, 26, 35, and 37. Mass 16 is again attributed to background  $\text{O}^-$  ions, mass 26 is  $\text{CN}^-$ , and masses 35 and 37 are  $(\text{Cl}^{35})^-$  and  $(\text{Cl}^{37})^-$ . The  $\text{CN}^-$  intensity increases with time as the molecular beam is first turned on. After a period of about 15 minutes it seems to reach a steady state. However, the  $\text{CN}^-$  to  $\text{Cl}^-$  ratios taken when decreasing the surface temperature between successive measurements are not reproducible when the temperature is increased. Table 2 gives the results of measurements taken when decreasing and when increasing the temperature between measurements.

TABLE 2

 $I_{CN^-}/I_{Cl^-}$  FROM CHLOROACETONITRILE  
 VERSUS SURFACE TEMPERATURE

Decreasing Temperature		Increasing Temperature	
T (°K)	$I_{CN^-}/I_{Cl^-}$	T (°K)	$I_{CN^-}/I_{Cl^-}$
2125	0.70	1958	0.24
2080	0.57	2024	0.42
2007	0.43	2138	0.45

Chloropicrin

Peaks in the mass spectrum due to the surface ionization of chloropicrin ( $CCl_3NO_2$ ) are observed at m/e of 16, 26, 35, 37, 42, and 46. Mass 16 is due to background  $O^-$  ions although there may be a very slight contribution due to the dissociation of the  $NO_2$  radical on the surface. Mass 26 is  $CN^-$ , masses 35 and 37 are  $(Cl^{35})^-$  and  $(Cl^{37})^-$ , mass 42 is probably  $CNO^-$ , and mass 46 is  $NO_2^-$ . Table 3 gives the relative intensities of the  $NO_2^-$ ,  $CN^-$ , and  $CNO^-$  ions relative to the intensity of  $Cl^-$  as a function of the surface temperature.

TABLE 3

RELATIVE INTENSITIES OF  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ , AND  $\text{CNO}^-$   
FROM CHLOROPICRIN VERSUS SURFACE TEMPERATURE

T (°K)	$\text{Cl}^-$	$\text{NO}_2^-$	$\text{CN}^-$	$\text{CNO}^-$
1907	1	0.0086	0.082	0.0059
2008	1	0.035	0.23	0.014
2131	1	0.18	0.54	0.035
2262	1	0.22	0.70	0.049

The  $\text{CN}^-$  peak is much more stable with time than the  $\text{CN}^-$  peak observed in chloroacetonitrile.

## CONCLUSIONS

### Chlorine

Because of the fact that the plot of  $I_{Cl^-}$  versus  $1/T$  (Figure 5) shows a maximum, it is concluded that at temperatures higher than  $2030^\circ$  K the ion emission from the filament is space charge limited. As the temperature of the surface is increased the electron emission increases and because of the low potential difference between the filament and  $A_1$  a space charge builds up in the region of the filament. This space charge tends to repel the ions away from the slit in  $A_1$ . The increase in ion emission with temperature is obscured and becomes a decrease above the temperature of the maximum. Since all of the negative ions studied exhibit a maximum intensity at a temperature of about  $2000^\circ$  K, this conclusion is further substantiated.

### Freons

Over a portion of the temperature range covered in these experiments, the straight lines in the plots in Figure 6 fit the experimental points fairly well. This combined with the low values of the intercepts suggests that the molecules are incompletely dissociated on the surface and

that the degree of dissociation, although not unity, is at least constant over some temperature interval. The change in slope at lower temperatures indicates that the degree of dissociation is changing in this temperature range. It should be noted that the straight line portion of the plots extends over a greater range of temperatures and that the fall off is less steep as the F to Cl atom ratio decreases.

It is not evident why the degree of dissociation should be constant at the higher temperatures when it is still less than unity. The increasing degree of dissociation at lower temperatures may be explained by considering the C-F and the C-Cl bond strengths. The average C-F bond strength is about 4.4 eV and the average C-Cl bond strength is about 3.3 eV. As the temperature increases the relative probability of breaking a C-F bond to that of breaking a C-Cl bond increases.

A degree of dissociation for each molecule may be calculated from the value of the intercept of the plot in Figure 6. If no assumptions are made as to the nature of the dissociation, then  $\alpha = [(m/n)_{\text{obs.}} / (m/n)_{\text{theory}}]$  gives a relative degree of dissociation in the temperature interval of its constancy. A reasonable assumption to make, however, is that the C-Cl bonds are completely broken. Then  $\alpha$  equals the degree of dissociation of the C-F bonds. Table 4 gives the results of calculating the degree of dissociation.

TABLE 4

DEGREE OF DISSOCIATION OF THE  
C-F BONDS IN FREONS

$CF_m Cl_n$	$\alpha$
$CF_3 Cl$	0.18
$CHF_2 Cl$	0.18
$CF_2 Cl_2$	0.23
$CFCl_3$	0.36

These results indicate that polyatomic molecules can be used at sufficiently high temperatures for determining electron affinity differences, although the results are not completely satisfying because of the incomplete dissociation observed.

Chloroacetonitrile

From the results of these experiments the conclusion is made that the electron affinity of the cyanide radical can not be accurately determined by the surface ionization of CN on tungsten. The variation of the  $CN^-$  ion intensity with time and the non-reproducibility of  $I_{CN^-}/I_{Cl^-}$  suggests that the CN radical is reacting with the tungsten, probably to form tungsten carbides. Since the  $Cl^-$  ion intensity does not vary with time, it seems that if a reaction on the surface to form tungsten carbides is taking place, then the

work function of the carbides must be essentially that of the pure tungsten.

From the data in Table 2, assuming a one to one ratio of CN radicals and Cl atoms on the surface, the electron affinity of the CN radical may be estimated. Using the value given by Bailey of 3.76 eV for the value of  $E(Cl)$ , the electron affinity of the CN radical is calculated from equation (16) assuming partition function ratios of unity. The range of  $E(CN)$  thus calculated is 3.2 eV to 3.7 eV. Bakulina and Ionov<sup>10</sup> report a value of  $E(CN)$  of  $3.7 \pm 0.2$  eV which they obtained by studying the surface ionization of KCNS molecules. It is quite possible that the range of values of  $E(CN)$ , that is the temperature dependence of the electron affinity, is due to the temperature dependence of the last term in equation (32). The accuracy of the data so far obtained preclude a meaningful analysis on the basis of this equation.

#### Chloropicrin

The data in Table 3 indicate that  $NO_2$  and CNO have high electron affinities. Curran<sup>14</sup> reports the value of  $E(NO_2)$  as greater than 3.6 eV and Farragher *et al.*<sup>15</sup> report a value of 4.0 eV. The indications of the present results are in qualitative agreement with these reported values. The electron affinity of the CNO radical has not been

obtained previously but these experiments indicate that it is about equal to that of fluorine.

If relative numbers of the neutral species evaporated from the surface could be determined, values of the electron affinities of  $\text{NO}_2$ ,  $\text{CN}$ , and  $\text{CNO}$  and information concerning their vibrational and rotational constants could be established.

#### Future Direction of Research

The sensitivity of these experiments and the ion current signal to noise ratios may be greatly increased by utilizing a pulsed molecular beam incident upon the surface and phase sensitive detection of the ion currents. A rotating blade beam chopper, which may be fitted into chamber 3, Figure 1, has recently been constructed, and successfully operated.

The use of different filament materials (e.g. carbon or rhodium) could stabilize the  $\text{CN}^-$  ion currents. The use of hafnium with its low work function of 3.5 eV would provide much greater sensitivity. With stable ion currents, increased sensitivity, and increased signal to noise ratios, vibrational and rotational constants for  $\text{CN}^-$  and other molecular negative ions might be evaluated from equation (32).

The use of molecules containing only the two electro-negative species of interest would greatly simplify the interpretation of the results; for example, HOCl, NO<sub>2</sub>Cl, and ClCN. However, such species are difficult to obtain in sufficient purity and are difficult to handle in a vacuum system.

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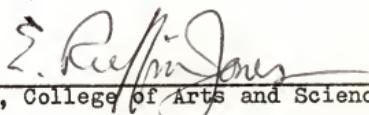
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#### BIOGRAPHICAL SKETCH

Charles Stephen Harden was born in Chattahoochee, Florida, on August 19, 1940. He was graduated from Wewahitchka High School, Wewahitchka, Florida in June, 1957. In September, 1957, he enrolled at Murray State College, Murray, Kentucky where he received a Bachelor of Science degree with majors in chemistry, physics, and mathematics in August, 1962. He entered the graduate school of the University of Florida in September, 1962, and was awarded the degree of Master of Science in August, 1964. Since September, 1962, he has held the position of graduate assistant in chemistry.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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